

May 5, 1953

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ANALYTICAL REAGENT AND METHOD

2,637,631

Filed March 9, 1949

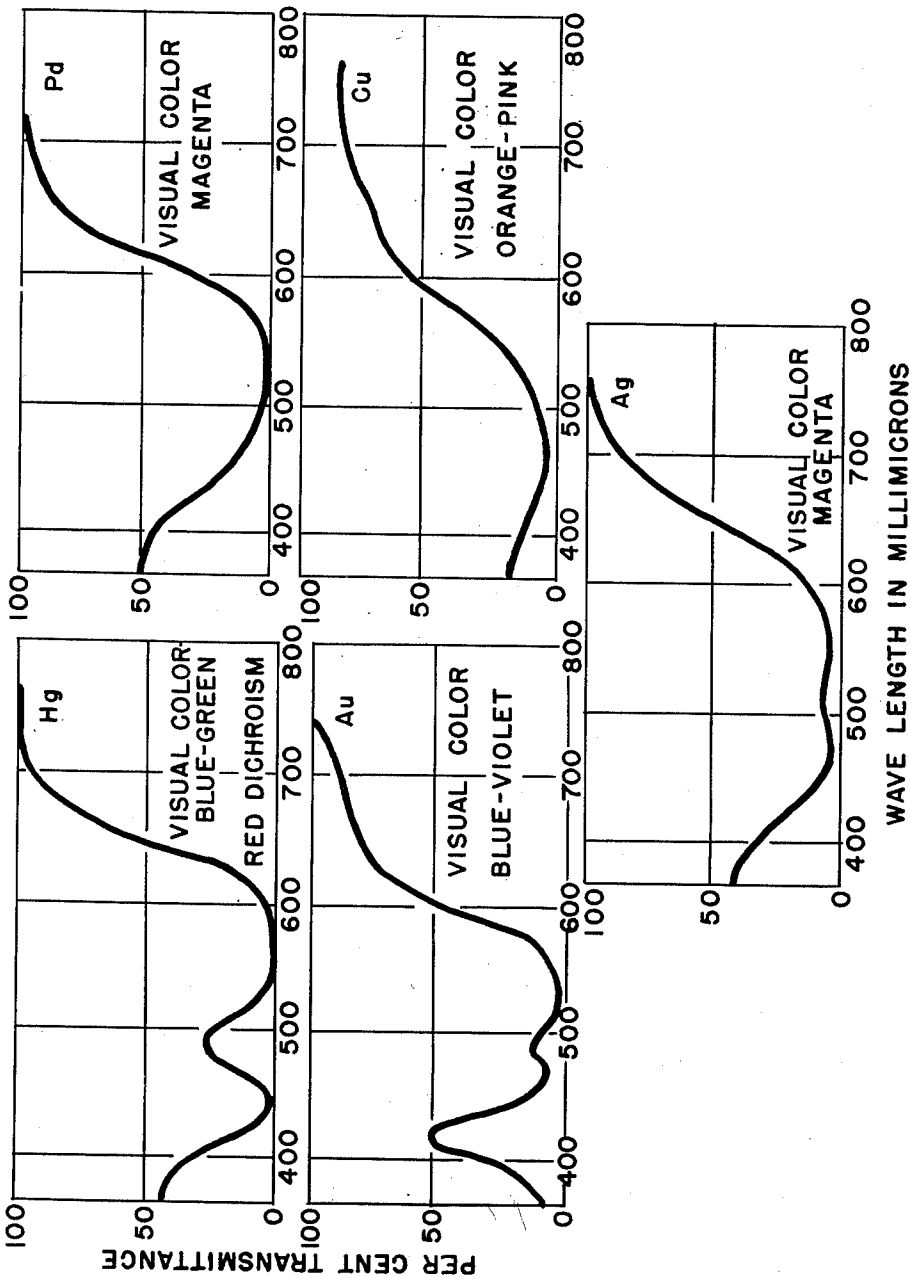


Fig. 1

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UNITED STATES PATENT OFFICE

2,637,631

ANALYTICAL REAGENT AND METHOD

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Application March 9, 1949, Serial No. 80,553

6 Claims. (Cl. 23—230)

(Granted under Title 35, U. S. Code (1952),
sec. 266)

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This invention relates to chemical analysis, particularly to a novel method involving the reaction of thio-Michler's ketone, (p,p'-bis(dimethylamino)thiobenzophenone), hereinafter referred to as TMK, with metallic ions, and to certain novel compounds resulting therefrom. The subject matter contained herein also disclosed in part in applicants' copending application, Serial No. 80,554.

One object of the present invention is to provide a novel method for detecting and determining trace amounts of certain metals.

A further object is to produce from the aforementioned method a novel means for determining trace amounts of cyanides and of carbon monoxide.

Other objects will more plainly appear from the detailed specification and drawing presented herewith in exemplification but not in limitation of the present invention.

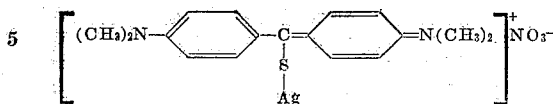
A clarification of one manifestation of the present invention is shown in the accompanying drawing, which illustrates diagrammatically in the figure absorption spectro-charts illustrating certain of the metallic compounds of the present invention.

During the investigation of color changes produced in the oxidation of a number of organic compounds it was found that TMK formed a compound of intense blue-green color when added to a mercuric chloride solution. The colored substance, surprisingly, was found to be a definite compound of TMK and mercuric chloride instead of an oxidation product, which it was first presumed to be. When the reaction was tried using salts of other metals it was found that similar compounds of different colors were obtained with cuprous salts of copper, and with salts of gold, platinum, silver, palladium, but not with salts of other metals. This selectivity of TMK for a certain group of metals to form intensely colored compounds indicated an entirely unexpected value as a reagent for inorganic analysis. This important, novel use of these colored metallic derivatives is unusually remarkable in view of the intensive search in the past two decades for suitable reagents for metallic ions.

TMK is a purplish-red crystalline substance, practically insoluble in water, but readily soluble in certain organic solvents to which it imparts a yellow color. It can be prepared: from dimethylaniline by treatment with thiophosphene; or by melting tetramethyldiaminodiphenylmethane and sulfur together; but preferably it is prepared from auramine by treatment with hydrogen sulfide.

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It has been assumed that the structure of the metallic derivatives of TMK would be typified by the following addition product with silver nitrate:



This assumption is based on the high intensity of color of these compounds in aqueous solution suggesting a structure closely resembling that assigned to diphenylmethane dyes. This is further borne out by the appearance of the crystallized metallic compounds, which are all deeply colored and exhibit the metallic reflex characteristic of intensely colored dye substances. Although the quinoid structure alone would account for the high color intensity of these substances, the metal content is an important factor, since the colors of the different compounds vary considerably according to the metal present in the compound. The mercury compound, for instance, as indicated in the figure, is blue-green with a strong red dichroism, the gold compound is purple, and the silver compound is magenta.

Chemically, the metal derivatives of TMK act as salts of the metal. Thus the mercury compound reacts quantitatively with cyanides, forming mercuric cyanide and free TMK. This reactivity permits the use of the colored complexes as internal indicators for volumetric analysis of metals or for a number of novel analytical methods in which the metals are used as reagents.

All the reagents used to demonstrate the present invention are standard C. P. chemicals, with the exception of TMK which was prepared at the Experimental Station of the E. I. du Pont de Nemours Company, Wilmington, Delaware. Analysis of this material showed the following composition:

	Found, Percent	Calculated, Percent
Nitrogen.....	9.8	9.85
Sulfur.....	10.9	11.27
Carbon.....	71.9	71.79
Hydrogen.....	7.1	7.09

Melting point, 195-200° C. (decomposition).

The minimum amounts of various metals in aqueous solution detectable visually when treated with TMK are determined as follows: 10 ml. of an aqueous solution containing a known amount of a salt of the metal being tested is buffered with 1 ml. of a 10% sodium acetate solution and then treated with 1 drop of 0.1% ace-

tone solution of TMK. The sodium acetate is added to prevent any traces of free Cl_2 in the water from reacting with the indicator. The test may be observed in a $\frac{3}{4}$ -in. test tube viewed from above and compared with a prepared blank. In making up the copper solutions cupric acetate is used; after buffering with sodium acetate a small quantity of hydroxylamine is added to obtain the cuprous state required for reaction with TMK. It is found that palladium solutions react slowly unless additional acetone (1 ml.) be added prior to the test.

The sensitivities found were:

	One part in
Hg -----	5,000,000
Ag -----	5,000,000
Cu(ous) -----	1,000,000
Au -----	1,000,000
Pd -----	10,000,000

The mercury compound is prepared by treating a saturated solution of TMK in acetone with an excess of 10% aqueous mercuric chloride solution. After standing for several hours the mercury compound is crystallized as deep colored, needle-like crystals with an intense green metallic reflex. Although the other metallic derivatives of the present invention are not obtained in crystallized form in the same manner, they are prepared by extracting the aqueous solutions with chloroform and evaporating the extract to dryness. Dark colored, microcrystalline deposits, resembling the mercury compound in appearance, are formed. The gold compound is also obtained as well defined crystals by mixing ether solutions of chloroauric acid and TMK. All of the solid compounds are found to be soluble to a limited extent in water and very freely in chloroform, alcohol, and acetone. Solubility in ether or aromatic liquids was negligible.

Aqueous solutions of the various metallic compounds of the present invention are prepared by reacting buffered solutions of the salts with an acetone solution of TMK until a depth of color suitable for spectrographic measurements is obtained. In each reaction the metal is maintained in excess of the TMK to prevent any interference from the yellow color of unreacted indicator. The light transmittance of these solutions may be measured throughout the visible spectrum, preferably by a Beckman spectrophotometer. The values obtained are plotted as shown in the figure. Observed visually, the aqueous solutions of the metallic compounds appear as follows:

Mercury—Blue-green, strong red dichroism
Silver—Rose-magenta
Copper—Orange-pink
Gold—Blue-purple, red dichroism
Palladium—Bluish magenta

These colors, indicated by the curves in the figure, are those of the aqueous solutions only. The same compounds in alcohol, acetone, or chloroform appear much redder in hue. However, the same absorption bands appear in the spectroscopy although they are much narrower and more sharply defined.

The analytical methods of the present invention that involve TMK are of added interest when applied to mercury, because of its novel use in the analysis of cyanides. As previously described herein, the novel blue-green compound formed with mercury is completely destroyed by cyanides; in the reaction mercuric cyanide is formed and the original TMK is regenerated. This reaction affords the use of TMK as an internal indicator

in a volumetric analysis method for mercury or cyanides. For example, solutions of both mercuric nitrate and potassium cyanide are prepared in 0.1, 0.01, and 0.001 molar concentrations. Before carrying out the titrations the solutions are buffered with sodium acetate and a few drops of a 0.1% solution of TMK in acetone are added. When mercury solutions are titrated with cyanide, the color change at the end point is very sharp with 0.1 and 0.01 molar solutions and sufficiently sharp with 0.001 molar solutions. When cyanide solutions are titrated with mercury, the color change is from pale orange to blue; the change shows the same degree of sharpness as the reverse titration.

Another example of this novel method for determining trace amounts of cyanides is as follows:

1. To a solution of sodium cyanide and water,
2. Add sodium acetate as a buffer;
3. Add 2-3 drops of a 0.1% solution of TMK in acetone;
4. Add a measured amount of a standard mercuric nitrate solution;
5. Stir the sodium cyanide solution and TMK mixture while adding the mercuric nitrate solution;
6. Stop adding mercuric nitrate when blue color, indicative of an excess of mercury, appears.

In all cases the results are reproducible and the end point is reversible. When accurately standardized solutions are used, it is found that the combining ratio of Hg to CN is exactly 1:2 in either direction. The presence of chlorides did not interfere with the reaction.

The herein described high color intensity and sharp absorption bands displayed by solutions of TMK in the presence of certain metals provides a novel indicator for colorimetric analysis of these metals. In this type of quantitative analysis, excess reagent must be used to insure complete conversion of all the metal to its colored complex. With TMK as the reagent any excess is preferably destroyed, or removed, to prevent interference by the yellow color due to the reagent itself. In the herein described reaction with mercury it was found that excess reagent could be removed by extraction with ether, leaving the blue-green mercury compound unaffected in the water layer.

Accordingly, the following novel colorimetric procedure is provided by the present invention: 10 ml. of a solution containing mercury ions is placed in a 30 ml. separatory funnel, together with 0.2 ml. of a solution made up of one part of glacial acetic acid and two parts of a 10% sodium acetate solution; the TMK (0.1% in alcohol) is added drop by drop until the blue-green color first formed becomes changed to a distinct reddish color, indicating a small excess of the TMK. After 10 seconds 6 ml. of ethyl ether is added and the mixture shaken thoroughly for a few minutes. The mixture is allowed to stand until the two layers completely separate, after which 5 ml. of the bottom layer is drawn off, preferably into a calibrated Klett-Summers colorimeter tube. A reading is taken, preferably with a Klett colorimeter fitted with a No. 56 filter having a transmission range of 540-590 millimicrons, which corresponds to the most marked absorption band of the mercury compound as indicated by the Hg curve in the figure.

The hereindescribed novel method will accurately determine micro traces of the various

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metals referred to herein. For example: determinations made of solutions containing 0.01, 0.05, 0.1, 0.3, 0.5, 1.0, 1.5, and 2.5 parts per million have been accurately determined. The determinations just quoted give a straight line curve when plotted on a coordinate chart that shows mercury concentrations in parts per million and colorimetric readings in scale units. This readily affords intermediate readings on micro amounts of mercury determined by this method.

Prior to the present invention there have been no satisfactory reagents for determining either macro or micro quantities of mercury by a simple procedure. Dithizone (diphenylthiocarbazon) and p-dimethylaminobenzalrhodanine, previously recommended for mercury determinations, have no quantitative significance except as limited colorimetric indicators and then only by following involved and uneconomical procedures. TMK, in the present invention, can be used not only as a colorimetric indicator but as an internal indicator in the volumetric analysis of mercury. This permits the general application of TMK to all analytical methods in which mercury can be used as a reagent.

The present invention also accomplishes the analysis of other herein described metals. The herein described silver complex, for example, is quantitatively destroyed by chlorides when the reaction is carried out in a solvent, such as alcohol, in which the solubility of silver chloride is below the limit of sensitivity of TMK to silver. Under these conditions solutions of chlorides can be titrated directly with standard silver nitrate solutions to a sharp end point, represented by a color change from pale yellow to magenta.

Furthermore, the present invention provides an important advance in the sensitive analysis of carbon monoxide. Prior to the present invention, in the previous palladium method, the gas containing carbon monoxide was passed into an excess of a standardized solution of palladous chloride, the reduced palladium filtered off, and the unused palladium salt measured gravimetrically as the dimethylglyoxime complex.

The present invention provides for the improved analysis of carbon monoxide in the following manner:

1. A measured amount of a mixture of air containing the suspected carbon monoxide is bubbled through a measured amount of a standard solution of palladium chloride and water;
2. A certain amount of the palladium is thereby reduced, if carbon monoxide is present;
3. Filter out and remove this reduced palladium;
4. Add a measured amount of TMK to the thus filtered solution and note the colorimeter reading of the resulting TMK color reaction therein;
5. Add an equal, measured amount of TMK to a second, or test amount of the standard palladium chloride solution identical to the first measured, or operation amount of that solution used in Step 1, and note the colorimeter reading of the TMK color reaction in said second solution;
6. The difference between these two colorimeter readings will indicate the amount of carbon monoxide originally present in the mixture of air tested.

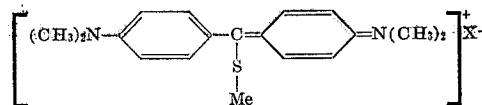
By this method minute traces of carbon monoxide, undetectable by prior methods, can be determined.

The absorption curve of the highly colored

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platinum compound, or platinum complex, closely resembles that of the silver compound or complex and that of the palladium compound or complex herein described and therefore is not shown on the figure. Platinum is readily detectable by the methods of the present invention, in dilutions equivalent to those recited herein for silver.

The structure of the herein described novel metallic derivatives of TMK may be generally exemplified by the following formula wherein Me represents an equivalent of any one of the metals in the group comprising mercury, copper, silver, gold, platinum, and palladium, and wherein X represents an equivalent of a negative radical, such as, for example, a nitrate, a sulphate, or a chloride:



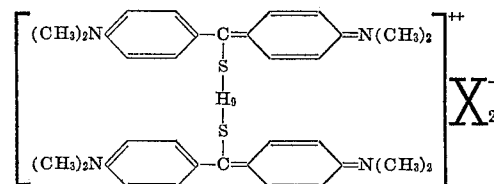
While preferred embodiments of the present invention have been illustrated herein, it is intended that the present invention shall include all embodiments and modifications within the spirit and scope of the appended claims. The invention described herein, if patented, may be manufactured and used by or for the Government for governmental purposes without the payment to us of any royalty thereon.

We claim:

1. The method of determining the concentration of metals of a single member of the group consisting of mercury, copper, silver, gold, platinum and palladium which comprises adding p,p'-bis(dimethylamino) thiobenzophenone to a solution suspected of containing the single member of the said metals in the form of ions of the group consisting of mercury, cuprous copper, silver, gold, platinum and palladium, identifying the metal by the color of the resultant product, and determining the transmissivity of the solution to light which is a function of the concentration.

2. The method of determining the concentration of mercury which comprises adding p,p'-bis(dimethylamino) thiobenzophenone to a solution suspected of containing mercury ions, identifying the metal by the color of the resultant product, and determining the transmissivity of the solution to light which is a function of the concentration.

3. A composition of matter consisting of an organic compound of the formula:



Where X is an equivalent of a negative inorganic radical.

4. A method of determining the concentration of mercury solutions and cyanide solutions wherein the concentration of one of the solutions is known which comprises adding p,p'-bis(dimethylamino) thiobenzophenone to a known amount of the mercury solution, thereby coloring the solution, titrating the solution with the cyanide solution until the said color disappears.

5. In the method of qualitatively determining the presence of chemical elements in a medium by producing a color change in said medium, the

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step which comprises adding p,p'-bis-(dimethyl-amino) thiobenzophenone to a solution containing a single ionic member of the group consisting of mercury, cuprous copper, silver, gold, platinum and palladium in a sufficient quantity to affirm the presence of one of said members and identifying the metal by the resultant color of the solution.

6. The method of detecting the presence of a metal according to claim 5 wherein the solution is suspected of containing mercury ions.

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